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Interaction of Sb(III) with iron sulfide under anoxic conditions: Similarities and differences compared to As(III) interactions

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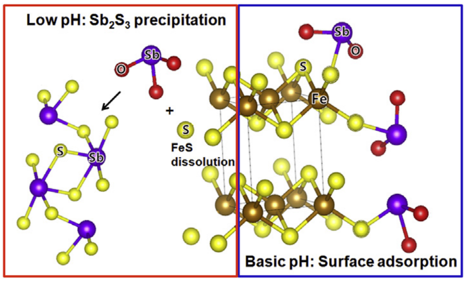
HIGHLIGHTS

- Interaction of Sb(III) with FeS was tested under acidic and basic pH conditions.
- The reaction mechanisms of Sb(III)–FeS and As(III)–FeS were compared.
- In both Sb(III)- and As(III)–FeS systems, pH was revealed as an important controlling parameter.
- Under acidic conditions the dominant reaction process was precipitation of as sulfide minerals.
- Surface complexation was the dominant reaction process under basic pH conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

This study examined the reaction mechanism of arsenite, As(III), and antimonite, Sb(III), with iron sulfide and compared their pH-dependent reaction behaviors under strictly anoxic environments. The comparison of Sb(III) with As(III), based on their chemical similarity, may provide useful insight into understanding the geochemical behavior of the less studied Sb(III). The pH-dependent batch sorption studies revealed that As(III) and Sb(III) displayed similar removal trends with pH in terms of the removal efficiency. However, the aqueous As(III) species transformed to thioarsenite species, while aqueous Sb(III) species remained inert under the highly sulfidic anoxic system. An X-ray absorption spectroscopy study demonstrated the reaction of As(III) and Sb(III) at acidic pH was closely related to the precipitation of sulfide minerals As_2S_3 and Sb_2S_3, respectively, as a consequence of the reaction with sulfide produced through mackinawite dissolution. Meanwhile, the removal at basic pH was inferred as a surface reaction, possibly through surface complexation, surface-precipitation, or both. In this study, the pH-dependent Sb(III) uptake mechanisms proved to be similar to the corresponding mechanisms for As(III) uptake, with mackinawite demonstrating a superior capacity to scavenge Sb(III) in ferrous and sulfide-rich reducing environments.

1. Introduction

Antimony (Sb) has increasingly received attention as an emerging pollutant in water and soil environments. Antimony

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contamination in soil is commonly found in the vicinity of smelters, mining sites, shooting ranges, and road sides (Filella et al., 2002). Increasing industrial need for Sb in the manufacture of flame retardants, catalysts, pigment, batteries, diodes and small arms, exacerbates the potential for Sb contamination in soil (Carlin, 2000; Filella et al., 2002; Guo et al., 2014). Antimony has been declared a pollutant of priority interest to the USEPA and Council of the European Communities adopted the maximum contaminant level (MCL) of Sb as 0.005 mg/L and 0.006 mg/L, respectively. In 2015, the South Korea Ministry of Environment also included Sb in the list of the Water Quality and Aquatic Ecosystem Conservation Act, planned to come into effect in January 2019 (MOE, 2015).

Antimony species generally exist as metalloids in natural water environments and are often considered to behave in a similar manner to arsenic (As), a metalloid historically regarded as one of the major toxic contaminants (Gebel, 1997; Mitsunobu et al., 2006). Since the orbital electron configurations of both As and Sb are the same, with s^2p^3 in their outermost shell, they display a wide range of oxidation states (−3 to +5) and most commonly exist as either a trivalent or pentavalent oxyanion (Wilson et al., 2010). The uncharged trivalent As and Sb species, $As(OH)_3^0$ and $Sb(OH)_3^0$, predominate in naturally reducing environments and both As and Sb have removed from aqueous solution or have removed after being oxidized to As(V) or Sb(V) through adsorption to metal oxide-based sorbents (Thanabalasingam and Pickering, 1990; Shotyk et al., 2005; Xu et al., 2011; Ilgen and Trainor, 2012). The interactions of $Sb(OH)_3^0$ species with sulfide species are also important in understanding the behavior of Sb, particularly in naturally reducing environments (Wilson et al., 2010). Note that, hereafter, As(III) or Sb(III) is used as a term for a trivalent arsenic oxoanion (arsenite) or a trivalent antimony oxoanion (antimonite), and does not refer to a form bonded to an element other than oxygen.

Among sulfide mineral species ubiquitously found in natural reducing environments, iron sulfide (FeS) in controlling As(III) has been intensively studied (Farquhar et al., 2002; Wolthers et al., 2005b; Gallegos et al., 2007; Gallegos et al., 2008; Han et al., 2011a). Arsenic(III) may form outer-sphere surface complexes or precipitate as arsenic sulfides, orpiment (As_2S_3) or realgar (AsS) (Farquhar et al., 2002; Wolthers et al., 2005b; Gallegos et al., 2008; Han et al., 2011a, 2011b). Han et al. (2011b) revealed the importance of pH on the reaction mechanisms of As(III) with nanoparticulate FeS. In their X-ray absoption spectroscopy (XAS) experiments, nano-particulate FeS reduced As(III) further to As(II) in the form of realgar (AsS) at pH 5. The mineral realgar was the main reaction product at pH 5, while mackinawite (crystalline FeS) formed surface complexes with As(III), as thioarsenite species, at pH 9. Kirsch et al. (2008) observed the fast reduction of Sb(V) to Sb(III) at the mackinawite surface at pH around 4. They found through Sb K-edge XAS analysis that both Sb(V) and Sb(III) formed amorphous or nano-particlulate SbS_3-like solids. Yet little is known about the interaction of Sb(III) with mackinawite and amorphous FeS minerals under wider pH ranges. To the best of our knowledge, no previous study has investigated the reaction mechanisms of Sb(III) in FeS under neutral or basic pH conditions.

In this study, the interaction of As(III) and Sb(III) with FeS was studied under varying pH conditions using laboratory batch and spectroscopic experimental methods. The objectives of this study were to understand the reaction mechanisms of As(III) and Sb(III) removal by FeS, under anaerobic conditions. X-ray absorption and X-ray photoelectron spectroscopy (XPS) were used to characterize the As(III) and Sb(III) species, as well as FeS, in the solid phase after reaction. The similarities and differences between As (III) and Sb(III) interactions with FeS are discussed.

2. Materials and methods

2.1. Batch experimental study

The methods of synthesizing FeS used in this study have been previously described (Han et al., 2011b). All the experiments in this study, including synthesis of FeS and preparation of spectroscopic study samples, were performed in an anaerobic glovebox under a gas phase of 98% N_2/2% H_2. All solutions were made up using N_2 purged, deoxygenated distilled water (DI-water).

The pH-dependent As(III)/Sb(III)-sorption tests were conducted using FeS over the range of pH 2 to 12. One milliliter of 10 g/L FeS suspension, 8.9 mL of 0.1 N NaCl solution (as a background electrolyte), and 0.1 mL of 1.3×10^{-1} M $NaAsO_2$ As stock solution or 4.1×10^{-2} M $C_8H_4K_2O_{12}Sb_2 \cdot 3H_2O$ (potassium antimonyl tartrate trihydrate, PAT) Sb stock solution were placed in 15 mL polypropylene tubes to achieve an As(III) or Sb(III) concentration of 150 mg As(III)/L or 500 mg Sb(III)/L (4.1×10^{-3} M) Sb(III). Various quantities of 0.8 N HCl and 1 N NaOH solutions were added to each tube to adjust the pH and total volume of each tube was adjusted to 15 mL with DI-water.

The prepared reaction tubes for pH-dependent sorption experiments were mixed with an end-over-end rotator for 3 days. After 3 days, half of the supernatant was filtered through a 0.1 μm nylon filter, diluted, and then acidified with concentrated HNO_3 and analyzed for total As and Sb by inductively coupled plasma optical emission spectroscopy (ICP-OES, Ultima 2, Horiba). The other half of the supernatant was used for aqueous speciation using a Bond Elut C18 cartridge (Agilent Technology), in order to measure the amount of non-polar As(III)/Sb(III) and other As/Sb species. The details of the speciation methods can be found in Yu et al. (2002). They revealed solution pH of 4 or higher gave best separation of Sb(III) and Sb(V). Therefore, the pH of the sample used for As/Sb speciation was adjusted to pH 5.5 using an acetate buffer solution mixed with ammonium pyrrolidine dithiocarbamate (APDC) to form a solid complex of As(III)/Sb(III) species. All batch experiments were performed at least in duplicate. Note that the initial Sb solution prepared with PAT were mostly trivalent in solution at acidic and neutral pH conditions and pentavalent fraction started to be detected when pH became 10 or higher. The results of pH-depenent Sb fraction were presented in Supplemental Materials (SM) Fig. 1.

2.2. Spectroscopic study

To study solid-phase speciation after reaction, 5 g/L of FeS (5.7×10^{-2} M) and 1 g/L As(III) or Sb(III) were reacted at pH 5, 7 and 9. Each batch was buffered using 0.1 N buffer solution:sodium acetate for the pH 5, 3-(N-morpholino)propanesulfonic acid (MOPS) for the pH 7, and N-Cyclohexyl-2-aminoethanesulfonic acid (CHES) for the pH 9. After reaction with As(III)/Sb(III) solutions for 3 days, solid phase FeS was collected by filtration and dried inside an anaerobic glovebox for various spectroscopic investigations.

Mineralogical compositions of FeS after reaction were identified by x-ray diffraction (XRD) using dried FeS samples. X-ray diffractometer (D8 Advance, Bruker-AXS) analyses were performed to characterize the mineralogical properties of FeS reacted with As(III) using Cu Kα radiation and a LynxEye position sensitive detector. The diffraction pattern was collect from 10° to 70° 2θ, with a nominal step size of 0.02° and a time per step of 0.5 s, using a 0.3° divergence slit and 2.5° secondary Soller slit. Synchrotron based powder X-ray diffraction patterns of FeS reacted with Sb(III) were collected on the beamline 9B (HRPD) at PAL. The incident X-rays were monochromatized to wavelength of a 1.5179 Å using a double-crystal Si(111) monochromator. Diffraction patterns were collected in the 2θ range of 10–130.5°, with a step size of 0.02°. The